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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Self-Stable Lattices and the Molecular Weight Control
Thereof

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FA-0643

TITLE

SELF-STABLE LATTICES AND THE
MOLECULAR WEIGHT CONTROL THEREOF

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ABSTRACT

10 A graft copolymer characterized by carboxylic-acid or amine
functional macromonomers attached at a terminal end thereof to a polymeric
backbone, wherein the functional groups have been neutralized, which graft
copolymer was prepared in the presence of an oligomeric acrylic chain transfer
agent to control the molecular weight of the graft copolymer. Such graft
copolymers are useful in high performance coatings and paints.

FA-0643

TITLE**SELF-STABLE LATTICES AND THE
MOLECULAR WEIGHT CONTROL THEREOF**

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TECHNICAL FIELD

This invention relates to a graft copolymer, referred to as a self-stabilized latex, having neutralized carboxylic-acid or amino functionality in a graft segment thereof which stabilizes the aqueous graft copolymer in dispersion. In particular, the invention relates to the molecular weight control of the graft copolymer. The invention also relates to a process for preparing such a graft copolymer.

BACKGROUND OF THE INVENTION

Automobiles and trucks receive exterior finishes for several well known reasons. First, such finishes provide barrier protection against corrosion. Second, consumers prefer an exterior finish having an attractive aesthetic finish, including high gloss and excellent DOI (distinctness of image).

Coating compositions comprise one or more film-forming polymers. Acrylic polymers are typically linear polymers that cure, upon application, by reaction with crosslinking agents. However, the use of non-linear graft copolymers has been disclosed. For example, U.S. Patent No. 4,801,653 to Das et al. describes the use of hydroxy functional graft copolymers. Das et al. disclose grafting by a condensation reaction between epoxy groups of a glycidyl ester, contained in an acrylic polymer, and carboxy groups on at least a portion of vinyl monomers which are polymerized in the presence of the acrylic polymer.

In preparing graft polymers in general, various living polymerization methods have been disclosed for obtaining functional ended polymers by selective termination of living ends. Such functionally ended polymers may subsequently be attached to another polymer, that is, as so-called macromonomer "arms" on a polymeric backbone to form a comb or graft copolymer. Webster, in "Living Polymerization Methods," 251 SCIENCE 887 (22 February 1991) generally discloses living polymerization methods for preparing architectural forms of polymers, including graft and comb copolymers.

U.S. Patent No. 4,680,352 to Janowicz et al., U.S. Patent No. 4,722,984 to Janowicz, and PCT WO 87/03605 disclose the use of cobalt (Co)

chelates as chain transfer agents in free radical polymerization. The latter patents disclose that macromonomers prepared by cobalt chain transfer can be polymerized to produce graft copolymers which are useful in coating and molding resins, including high solid finishes and aqueous or solvent based finishes. The use of such polymers, however, have so far found only limited use in the automotive finishes area, as for example disclosed in U.S. Patent No. 5,010,140.

Water dispersible polymers are well known in the art and have been used to form waterbased coating compositions, pigment dispersions, adhesives and the like. Graft copolymers containing carboxyl groups and the preparation of these polymers is shown in Japanese Laid Open Patent Application (Kokai) No. 1-182304 dated July 20, 1989. This reference shows graft copolymers that have carboxyl groups and discloses side chains from acrylic and methacrylic acid that have hydrophilic properties. This reference further teaches the use tertiary alcohol-based ester units of acrylic or methacrylic acid to form a macromonomer which is used to form a graft copolymer and then is hydrolyzed to form carboxylic-acid groups on the polymer. The process taught by the reference is an inefficient process which does not form pure graft copolymer but results in a mixture of graft copolymer and low molecular weight components that are detrimental to pigment dispersions formed from the graft copolymer and finishes formed from such a composition.

BASF EP 0363723 describes an acid-functional acrylic copolymer dispersion for use in an OEM clear coat to be crosslinked with a melamine formaldehyde binder. The acrylic copolymer is prepared in a solvent in a two-stage process where the hydrophilic part (acid-functional monomer) is concentrated in one of the two stages. The overall copolymer is afterwards neutralized with an amine and dispersed in water. The difference between a one stage product is the solids/viscosity relation being most favorable for the two stage acrylic. A disadvantage of this technology is the fact that the hydrophilic part needs to be over 60% of acid functional monomer which could give problems in humidity resistance.

The present invention disclosed improved graft copolymers useful in aqueous coatings.

SUMMARY OF THE INVENTION

The present invention relates to a graft copolymer prepared from an acrylic copolymer macromonomer having at least 10%, based on the weight of

the macromonomer, of polymerizable alpha-beta ethylenically unsaturated monomers with either a carboxylic-acid or amino group. Such macromonomers suitably may have a weight average molecular weight (MW) of 500 to 30,000. About 2-98% (by weight) of the macromonomer is copolymerized with 98-2% of a blend of other alpha, beta-ethylenically unsaturated monomers to form a graft copolymer with a MW of at least 3000, in the presence of an oligomeric chain transfer agent, as described in more detail below. The graft copolymer can be formed by copolymerizing the backbone monomers in the presence of an aqueous dispersion of the macromonomer. The macromonomer can be neutralized before being dispersed in water.

It has been found that improved aqueous or waterborne coating systems are obtained by using these graft copolymers. Such compositions have the advantage of providing excellent coating properties desirable for an automotive finish.

One aspect of the present invention is directed to a graft copolymer having a weight average molecular weight of 3,000 to 500,000 comprising the reaction product of:

- (i) 2 to 98 percent, based on the weight of the graft polymer, of ethylenically unsaturated monomers for forming the polymeric backbone of the graft copolymer, and
- (ii) 98 to 2 percent, based on the weight of the graft polymer, of macromonomers capable of attaching to said polymeric backbone at a single terminal point of each macromonomer, said macromonomers comprising from about 10 to 100 percent, based on the weight of the macromonomer, of polymerized ethylenically unsaturated monomers containing a carboxylic or amino functionality and having a weight average molecular weight of about 500-30,000, such that the macromonomers are water soluble or dispersable when at least partially neutralized;
- (iii) 1.0 to 20 percent, based on the weight of the graft copolymer, of one or more oligomeric chain transfer agents having a terminal unsaturation like the macromonomer of

(ii) but having a substantially lower average molecular weight than the macromonomer of (ii) above;

wherein said carboxylic or amino functionality has been at least partially neutralized to form a stable dispersion of the graft copolymer, with the backbone mostly in particle form, in water or an aqueous carrier.

The present invention is also directed to aqueous dispersions (20 to 100 percent water) of the graft copolymer and coating compositions made with such graft copolymers. Such coatings compositions may further comprise 2 to 50 percent, based on the weight of the binder of a crosslinking agent which, when the composition is cured, can react and crosslink with said graft polymer; and 40 to 90 percent by weight, based on the weight of the composition, of an aqueous carrier comprising 20 to 100 percent water. Coatings may further comprise additional curable linear or branched film-forming polymers or binder materials, in various proportions. For example, the composition may comprise linear or branched hydroxy-functional acrylic, polyester, or polyurethane copolymers. Further binder materials, in relatively minor amounts, include, for example thickeners, adhesion promoters, etc.

The process for making the graft copolymer are also part of this invention.

The present invention offers several significant advantages. First, graft copolymers with acid or amine groups concentrated in one segment require less of these functional groups to get a stable dispersion, thus leaving fewer moisture sensitive groups when used in coatings.

Second, standard emulsions are stabilized by surfactants which besides remaining in the film as moisture sensitive residues, migrate to the coating interfaces and generate weak boundary layers which lead to poor adhesion and delamination. The surfactants also stabilize foam formed by trapped air during spraying, leading to pinholing. The graft copolymers of the present invention can be used in compositions made with lesser amounts of surfactants or even no surfactants.

Third, standard emulsions for which water is a non-solvent, need considerable solvent to allow coalescence (film formation) after being applied to a surface. This leads to higher VOC. In the present invention, the hydrophilic macromonomers which are on the surface of the self-stabilized lattices are plasticized by the water and allow film formation with little or no solvent, thus allowing coating compositions to be formulated with much lower VOC. These and

other advantages of the invention can be better understood by reference to the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

5 A water soluble or dispersible graft acrylic copolymer is disclosed which is formed by free radical initiated copolymerization of 2-98% (by weight) alpha-beta unsaturated monomers in the presence of an acrylic macromonomer. The acrylic macromonomer is ionic in character with an average number
10 molecular weight (MN) of between 500 to 30,000 and containing at least 10% of an acid or amino functional alpha-beta unsaturated monomer. After at least partial neutralization of the carboxyl or amino groups with, for example, an amine in the case of carboxyl groups, these acrylic resins form stable solutions or
15 dispersions in water.

 These graft copolymers form particles, either alone or in aggregate,
15 in dispersions or coating compositions. The macromonomers are relatively hydrophilic and hence soluble or dispersible in the aqueous carrier, and the polymeric backbone (to which the macromonomers are attached) is relatively water insoluble. Such particles may be crosslinked or uncrosslinked, for example by means of diacrylate monomeric units, and suitably have an average particle
20 size of 50 to 1000 nanometers (nm), preferably 100 to 250 nm.

 The molecular weight of the self-stable latex is controlled during polymerization by utilizing oligomeric chain transfer technology as hereafter described. This involves very low molecular weight vinyl terminated oligomers as radical chain transfer agents in the polymerization of desired monomers with
25 higher molecular weight macromonomer (emulsion stabilizer).

 The oligomer chain transfer agents are generally a distribution of molecular weights that have a very low degree of polymerization, for example, DP=2 to 8. These low molecular weight macromonomers differ from the macromonomers used to stabilize the emulsion particle in that (1) they are
30 comprised of an average molecular weight lower than the stabilizer macromonomers themselves, (2) the oligomer macromonomers will not, or to a substantially less extent or degree, provide emulsion stability as does the macromonomer stabilizer, and (3) they typically contain little or no functional groups which might provide water solubility to the oligomer.

35 For example, a macromonomer stabilizer having an average composition of 60% methymethacrylate and 40% methacrylic acid and a

number average molecular weight of 1200 might be used along with an oligomer chain transfer agent comprised of 100% methylmethacrylate having a molecular weight of M_n equal to 315. The neutralized 60/40 macromonomer becomes the grafted emulsion stabilizer. The oligomer, which cannot be neutralized, could
5 not act as an emulsion stabilizer and can only be used in conjunction with the 60/40 macromonomer to form stable low molecular weight self-stable emulsions.

The chain transfer process, by definition, terminates the growing radical chain but does not change the kinetic chain length. The end result is the production of several, and possibly hundreds, of polymer chains from one
10 initiating radical. The initiating radical, from a polymerization initiator, can be taken for any common class of initiator such as azo, peroxide, peroxyester, or similar classes of thermal initiators as well as redox and photo-initiators.

Oligomeric chain transfer agents, much like other conventional transfer agents, become incorporated into the polymer during the polymerization
15 process. One advantage is that the oligomer compositions do not introduce moieties which can degrade the properties of the final copolymer. In comparison, the use of conventional sulfur-containing transfer agents produce polymers which contain groups less durable than the polymer being synthesized. They often leave the resin with an offensive odor. Some cobalt chain transfer
20 agents are active in water based polymerizations as long as the bulk of the monomers are methacrylates. If self-stable latices require the use of acrylate and styrene monomers in the backbone, then cobalt chain transfer agents may not be very effective. Cobalt catalysts also have the disadvantage of not working well with hydroxyl and/or carboxyl containing monomer. This is not a factor with the
25 oligomer transfer agents.

As mentioned above, one important aspect of using oligomer chain transfer agents for molecular weight control is that, in making the self-stable latex, the oligomers do not contribute to the particle stability in the same way as the stabilizer macromonomers. Since the oligomers are hydrophobic, either as an
30 end group, due to chain transfer, or as a short graft, due to co-polymerization, they contribute to the hydrophobic portion of the polymer.

The stabilizer macromonomers are in themselves transfer agents as defined by the mechanism for addition-elimination chain transfer. One can observe a limited reduction in molecular weight by solely increasing the number
35 of moles of stabilizer macromonomer in the self-stable latex composition. The oligomer transfer agents, because of their low molecular weight, provide a novel

way of increasing the number of moles of vinyl-terminated macromonomer in the process, hence a larger concentration of molecular weight control agent, with a minor impact on hydrophobic-hydrophilic balance in the polymer composition.

The competition between oligomer incorporation and beta-scission (chain transfer) defines the relative activity of the oligomer transfer agents and is largely controlled by three factors: (1) temperature -- the higher the temperature of the polymerization, the more chain transfer, (2) backbone monomer composition -- acrylates and styrene will provide competing mechanisms for chain transfer and incorporation while methacrylates only undergo chain transfer, and (3) concentration of oligomer versus monomers in reactor -- the higher the relative molar concentration of oligomer versus (meth)acrylate and/or styrene monomers in the reactor during the polymerization, the larger the molecular weight reduction.

Oligomer chain transfer agents reduce the variables that narrow the utility of commercial chain transfer agents or techniques that are commonly used to control molecular weight. It works with a wide variety of monomers and initiator types without adversely affecting other important polymer properties. For example, it provides for the introduction of acceptable monomer units into the polymer that are commonly considered, by those knowledgeable in the art, as contributing a neutral to positive effect toward artificial and natural weathering durability. Having control over the molecular weight of a self-stable latex provides an additional variable for particle coalescences in film formation in addition to other conventional variables such as co-solvents, particle size, polymer glass transition temperature and temperature.

The graft copolymer of the present invention is useful in coating compositions. Such compositions suitably comprise about 20 to 98 percent, preferably 50 to 90%, based on the weight of the binder, of the specified graft polymer. (In general, the total polymeric and oligomeric components of a coating composition are conventionally referred to as the "binder" or "binder solids" and are dissolved, emulsified or otherwise dispersed in the aqueous liquid carrier. The binder solids generally include all the normally solid polymeric components of the composition. Generally, catalysts, pigments, or chemical additives such as stabilizers are not considered part of the binder solids. Non-binder solids other than pigments usually do not amount for more than about 10% by weight of the composition.)

Coating compositions, according to one aspect of the present invention, suitably contain about 10-60%, more typically 50-70% by weight of the binder, and about 40-90%, more typically 50-30% by weight, of an aqueous carrier.

5 The graft copolymer itself contains about 2-98%, preferably 5-40%, and most preferably 15-40% by weight of macromonomer arms and correspondingly about 98-2%, preferably 60-95%, most preferably 60-85% by weight of backbone polymer. The graft copolymer has a weight average molecular weight of about at least 3,000, preferably 20,000 to 500,000, most
10 preferably 20,000 to 300,000. The side chains of the graft copolymer are formed from relatively water soluble macromonomers that have a weight average molecular weight of about 500-30,000 and preferably 2,000-10,000 and contain about 10-100% by weight and preferably 15-40% by weight, based on the weight
15 of the macromonomer, of polymerized ethylenically unsaturated acid or amino monomers which are then at least partially neutralized. These side chains are relatively hydrophilic and keep the graft polymer well dispersed in the resulting coating composition.

 The backbone of the graft copolymer is hydrophobic relative to the side chains, but can contain polymerized ethylenically unsaturated acid or amine
20 monomers or salts thereof. The backbone may contain polymerized monomers selected preferably from the group consisting of acrylates and styrene, but may contain up to 50% alkyl methacrylates. It may also contain up to 50% by weight, based on the weight of the graft copolymer, of polymerized ethylenically unsaturated non-hydrophobic monomers which may contain functional groups in
25 addition to the amino or acid groups. Examples of such monomers are hydroxy ethyl acrylate, hydroxy ethyl methacrylate, acrylamide, nitro phenol acrylate, nitro phenol methacrylate, phthalimido methyl acrylate, and phthalimido methacrylate. Still other vinyl monomers can be incorporated into the backbone, e.g., ethylenically unsaturated sulfonic, sulfinic, phosphoric or phosphonic acid and
30 esters thereof, such as styrene sulfonic acid, acrylamido methyl propane sulfonic acid, vinyl phosphonic acid and its esters and the like.

 In one embodiment, the waterborne acrylic graft copolymers contain 0-60 or more preferably 10-40 parts by weight of hydroxy functional acrylic monomers, e.g., 2-hydroxyethyl acrylate, 4-hydroxyethyl methacrylate, 2-
35 hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 4-hydroxybutyl acrylate,

and 4-hydroxybutyl acrylate. All or most of these may be present in the side chains and may serve as crosslinking sites.

As indicated earlier, the graft polymer comprises macromonomeric side chains attached to a polymeric backbone. Each macromonomer ideally
5 contains a single terminal ethylenically unsaturated group which is polymerized into the backbone of the graft copolymer and typically contains polymerized monomers of methacrylic acid, its esters, nitriles, amides or mixtures of these monomers.

The ethylenically unsaturated carboxylic-acid or amino functional
10 monomers, in an amount of at least 10% by weight of the macromonomers, can suitably include, as carboxylic-acid monomers, the following: methacrylic acid, acrylic acid, itaconic acid, maleic acid (or maleic anhydride which upon hydrolysis after polymerization gives maleic acid), and the like or mixtures thereof. Suitable amino functional monomers include t-butylamino ethyl methacrylate, diethyl
15 amino ethyl acrylate, diethyl amino ethyl methacrylate, and the like or mixtures thereof. The above acids or amines also can be used in the backbone of the graft copolymer, but usually in a lesser amount by weight than in the macromonomeric arms, in order to maintain the water-insolubility of the backbone. In this case, however, it is preferable that both the backbone and macromonomer arms should
20 comprise the same kind of monomer, either acid monomers or amino monomers.

In addition to the minimum amount of acid or amino functional monomers, up to 90% by weight, based on the weight of the macromonomer, of other polymerized ethylenically unsaturated monomers can be present in the macromonomer, for example, but not limited to acrylic and methacrylic acid
25 esters of straight-chain or branched monoalcohols of 1 to 20 carbon atoms. The majority of these monomers should be methacrylates, preferably 60-80% by weight of the macromonomer, for example, alkyl methacrylates having 1-12 carbons in the alkyl group can be used such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate,
30 pentyl methacrylate, hexyl methacrylate, 2-ethyl methacrylate, nonyl methacrylate, lauryl methacrylate and the like can be used. Cycloaliphatic methacrylates can be used such as trimethylcyclohexyl methacrylate, t-butyl cyclohexyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate, and the like. Aryl methacrylates such as benzyl methacrylate also can be used.

35 Ethylenically unsaturated monomers containing hydroxy functionality include hydroxy alkyl acrylates and hydroxy alkyl methacrylates,

wherein the alkyl has 1 to 12 carbon atoms. Suitable monomers include hydroxy ethyl acrylate, hydroxy propyl acrylate, hydroxy isopropyl acrylate, hydroxy butyl acrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, hydroxy isopropyl methacrylate, hydroxy butyl methacrylate, and the like, and mixtures thereof. Reactive functionality may also be obtained from monomer precursors, for example, the epoxy group of a glycidyl methacrylate unit in a polymer. Such an epoxy group may be converted, in a post polymerization reaction with water or a small amount of acid, to a hydroxy group, or with ammonia and/or a primary amine to give a hydroxy amine.

Suitable other olefinically unsaturated comonomers include: acrylamide and methacrylamide and derivatives as alkoxy methyl (meth) acrylamide monomers, such as methacrylamide, N-isobutoxymethyl methacrylamide, and N-methylol methacrylamide; itaconic and maleic anhydride and its half and diesters; vinyl aromatics such as styrene and vinyltoluene; polyethylene glycol monoacrylates and monomethacrylates; aminofunctional (meth) acrylates as, e.g., diethylaminoethylmethacrylate and t-butylaminoethylmethacrylate; glycidyl functional (meth) acrylates as glycidylmethacrylate.

Other functional monomers as acrylonitrile, acroleine, allyl methacrylate, aceto acetoxyethyl methacrylate, methylacryl amidoglycolate methylether, ethylene ureaethyl methacrylate, 2-acrylamide-2 methyl propanesulfonic acid, trialkoxy silyl propyl methacrylate, reaction products of mono epoxyesters or monoepoxy ethers with alpha-beta unsaturated acids and reaction products of glycidyl (meth) acrylate with mono functional acids up to 22 carbon atoms.

The above monomers also can be used in the backbone of the graft copolymer.

The graft polymer may be prepared by polymerizing ethylenically unsaturated monomers in the presence of macromonomers each having a terminal ethylene unsaturation for grafting. The resulting graft polymer can be envisioned as being composed of a backbone having a plurality of macromonomer "arms" attached thereto. In the present composition, both the macromonomer arms and the backbone may have reactive functionalities capable of reacting with a crosslinking compound or polymer, although it is optional to have such reactive functionalities only on the macromonomers. It is to be understood that the macromonomers referred to as having carboxylic or amine

functionality may be part of a mixture of macromonomers of which a portion do not have any carboxylic or amine functionality in variable amounts of carboxylic or amine functionality. It is also understood that, in preparing any macromonomers, there is a usually a normal distribution of functionality.

5 To ensure that the resulting macromonomer only has one terminal ethylenically unsaturated group which will polymerize with the backbone monomers to form the graft copolymer, the macromonomer is prepared by using a catalytic chain transfer agent. Typically, in the first step of the process for preparing the macromonomer, the monomers are blended with an inert organic
10 solvent which is water miscible or water dispersible and a cobalt or other chain transfer agent and heated usually to the reflux temperature of the reaction mixture. In subsequent steps, additional monomers and chain transfer agent and conventional polymerization catalyst are added and polymerization is continued until a macromonomer is formed of the desired molecular weight.

15 The term "macromonomer" is used herein to describe polymers of limited chain length or molecular weight which have such terminal olefinic moieties. The present macromonomers have about 10 to about 300 monomeric units linked to the end group, the units being independently selected from the monomeric units described below. The number average molecular weight can
20 vary from about 1000 to 50,000, preferably 1,000 to 10,000.

 The concentration of vinyl terminal macromonomers is at least about 80 mol %. Preferably, concentrations of at least about 85 mol %, more preferably at least about 90 mol %, most preferably at least about 95 mol % and any and all concentrations and ranges of concentrations therebetween, and up to
25 about 100 mol % are contemplated.

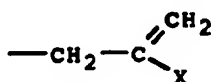
 The macromonomers can be produced by a cobalt chain transfer agent, as described in copending U.S. Patent Application S.N., herein incorporated by reference in its entirety. The macromonomers can also be produced by a process which employs, as a free radical chain transfer agent,
30 relatively low molecular weight oligomers having ω -unsaturation (which oligomers are, in fact, themselves macromonomers of a relatively limited degree of polymerization or chain length). These oligomers may themselves be made with a metal chelate or other suitable chain transfer catalyst. However, although less preferred, it is contemplated that ω -unsaturated oligomers, having at least
35 two monomeric units, might also be prepared without polymerization, according to a known or routine organic synthesis. Hence, the term "oligomer" or

"oligomeric" does not herein connote a compound necessarily prepared by polymerization.

The oligomeric chain transfer agents employed in the present invention may be a pure compound or a polydisperse mixture of compounds. These materials have utility either alone or as blends when used as chain transfer agents for virtually any free radical polymerization.

Preferably, the present chain transfer agents are used as a polydisperse mixture, which mixture has a distribution of molecular weights having a very low degree of polymerization, i.e., DP = 2 to 100, preferably 2 to 20, and most preferably 2 to 7.

The oligomer chain transfer agents of interest, as well as the polymers or macromonomers produced thereby, include those having the following end group:



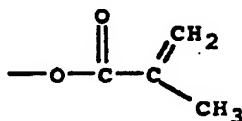
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where X is -CONR₂, -COOR, OR¹, -OCOR, -OCOOR¹, -NR¹COOR¹, halo, cyano, or a substituted or unsubstituted phenyl or aryl, wherein each R is independently selected from the group of hydrogen, silyl, or a substituted or unsubstituted alkyl, alkyl ether, phenyl, benzyl, or aryl, wherein said groups may be substituted with epoxy, hydroxy, isocyanato, cyano, amino, silyl, acid (-COOH), halo, or acyl; and wherein R¹ is the same as R except not H; wherein each alkyl is independently selected from the group consisting of branched, unbranched, hydrocarbons having 1 to 12, preferably 1-6, and most preferably 1-4 carbon atoms or cyclical hydrocarbons having 4-12, preferably 4-6 carbon atoms; halo or halogen refers to bromo, iodo, chloro and fluoro, preferably chloro and fluoro, and silyl includes -SiR²(R³)(R⁴) and the like, wherein R², R³, and R⁴ are independently alkyl, phenyl, alkyl ether, or phenyl ether, preferably at least two of R², R³, and R⁴ being a hydrolyzable group, more preferably two of which are alkyl ether, wherein alkyl is as defined above, preferably methyl or ethyl. A plurality of silyl groups may be condensed, for example, an organopolysiloxane such as -Si(R²)₂-O-Si(R³)₂R⁴, wherein R², R³, and R⁴ are independently alkyl. See U.S. Patent 4,518,726, hereby incorporated by reference, for further exemplification of silyl groups in general.

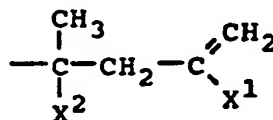
A preferred class of oligomeric chain transfer agents for use in the present invention are those oligomers according to the above structure in which X is $-\text{CONR}_2$, $-\text{COOR}$, unsubstituted or substituted phenyl, aryl, halo, or cyano, and R is as defined above.

5 A more preferred class of oligomeric chain transfer agents for use in the present invention are those oligomers according to above structure in which X is $-\text{COOR}$ or phenyl and R is hydrogen, alkyl or phenyl unsubstituted or substituted with epoxy, hydroxy, or alkoxyethyl.

10 The oligomers employed in the present invention are to be distinguished from the more conventional oligomers having the following end group:



15 Preferably, the oligomers employed in the present invention, as well as the polymers produced thereby, are characterized by the following end group:

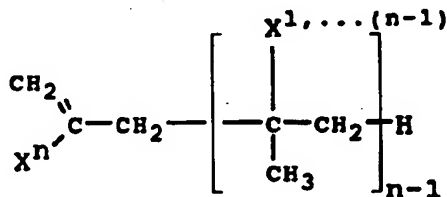


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wherein X^1 and X^2 are independently (the same or different) X as defined above.

The general chemical structure of suitable oligomers for use in the present invention is described below where $n = 2$ to 100 on average.

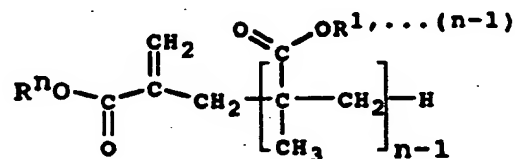
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wherein X^1 to X^n is independently defined as above for X and n is on average 2 to 100, preferably 2 to 20.

For example, a general formula for a methacrylate oligomeric chain transfer agent is as follows:

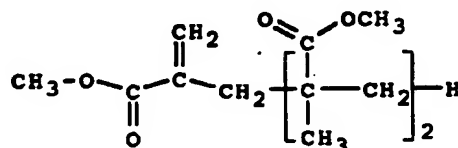
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wherein R^1 to R^n are independently (the same or different) and defined as above for R and n is on average 2 to 20, preferably 2 to 7.

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As a further very specific example, a methyl methacrylate trimer, wherein n equals 3 and R equals $-CH_3$, is as follows.



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As indicated above, dimers, trimers, tetramers, etc., as defined above, or mixtures thereof, are suitably employed in the present invention. Mixtures of varying molecular weight are probably easier to prepare in large quantities. A wide range of molecular weight oligomers may be made, which in turn may be distilled to obtain a purer or pure oligomer, for example the tetramer. The oligomers do not have to be in any particular form. The oligomers may be stored and added in bulk, as liquids or solids, mixed in a solvent, mixed with monomers.

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Many of the oligomers that can be employed in the present process, are known, for example as taught in Janowicz published European Patent Application 0 261 942, herein incorporated by reference. The alpha-methyl styrene dimer, which is the same as the compound 2,4-diphenyl-4-methyl-1-pentene, is known as a chain transfer agent. However, chain transfer agents with such a phenyl or aryl group may be less preferred for reasons of the properties of the resulting polymers as a consequence of the presence of aromatic end groups derived from the chain transfer agent. It may be

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preferred to exclude or reduce the amount of the dimer ligomer, where n equals 2 in the above formulas, because such dimer may be somewhat less reactive than other oligomeric chain transfer agents.

According to the present invention, suitable oligomeric chain transfer agents are dimers, trimers, tetramers, and higher oligomers of monomers and mixtures thereof. Thus, oligomers comprising branched, unbranched or cyclical alkyl or aromatic methacrylates such as methyl, ethyl, propyl, butyl, 2-ethylhexyl, and/or decyl methacrylate; cyclohexyl, phenyl, or benzyl methacrylate; functional alkyl or aromatic methacrylates such as glycidyl methacrylate, hydroxyethyl or hydroxypropyl methacrylate, methacrylic acid, methacrylonitrile, methacrylamide, 2-isocyanatoethyl methacrylate, dimethylaminoethyl methacrylate, N,N-dimethylamino-3-propyl methacrylamide, t-butylaminoethyl methacrylate, and silanes such as methacryloxypropyltrimethoxysilane, or mixtures of the foregoing, and numerous others can be employed. Hetero-oligomers, as for example, the reaction product of methylmethacrylate and methacrylonitrile are suitable. These oligomers are most easily made by a metal chelate catalytic chain transfer, for example a cobalt chelate, as will be explained below, but they could be made by other methods as well.

The present oligomeric chain transfer agents can be used to control molecular weight during polymerization of the graft copolymer of the present invention, the macromonomers used in forming the graft copolymer, and/or the backbone used in forming the graft copolymer. The chain transfer agent can be used in an effective amount of only a few percent by weight of the reactants. A suitable range of oligomeric chain transfer agent is between 0.01% and 80% by weight, preferably about 0.1 to 40%, and most preferably 1 to 10% by weight of the monomer reactants.

The free radical polymerization of unsaturated monomers, some of which carry acid functional groups for stabilization may occur in suspension, emulsion or solution, in aqueous or organic media, as will be familiar to those skilled in the art.

The oligomeric chain transfer agents employed in the present invention are typically prepared by standard solution polymerization techniques, but may also be prepared by emulsion, suspension or bulk polymerization processes. Preferably, a metal chelate chain transfer catalyst is employed in the method of preparation. (In effect, one chain transfer agent is used to make another chain transfer agent.) Such a method is disclosed in the above

mentioned U.S. Patent No. 4,680,352, issued to Janowicz et al. and U.S. Patent No. 4,694,054, issued to Janowicz, both of which are commonly assigned and hereby incorporated by reference in their entirety, as well as WO 87/3605 published on 18 June 1987.

5 When employing a cobalt chelate in the preparation of the present oligomers, it may be feasible to remove cobalt as well as any color from the reaction product by precipitation with a solvent and the subsequent use of activated charcoal. For example, the addition of ethyl acetate (Rhone-Poulenc AR grade, 99.5%, 0.005% acetic acid) in various proportions has been found to
10 cause substantial precipitation of cobalt as a dark brown solid and therefore decreased color in the final solution. Other precipitating solvents include a mixture of acetone and water and a mixture of acetonitrile and water. Color may be further removed by classical techniques, for example, simple treatment with activated charcoal for about 15 minutes followed by filtration through a short
15 column packed with CELITE™ 545 filter aid.

For larger scale production, continuous (CSTR) production of the oligomer may be more economical.

In general, to obtain some of the relatively lower molecular weight oligomeric chain transfer agents of the present invention, one could employ
20 higher amounts of a metal chelate chain transfer agent than employed in the prior art for obtaining relatively higher molecular weight macromonomers. In other words, essentially the same prior art processes used in making low molecular weight macromonomers can be used in making the present relatively low molecular weight oligomeric chain transfer agents, such as dimers and
25 trimers.

An initiator which produces carbon-centered radicals, sufficiently mild not to destroy the metal chelate chain transfer agent, is typically also employed in preparing the oligomeric chain transfer agents. Suitable initiators are azo compounds, as described below.

30 As will be apparent to one skilled in the art, these oligomers could also be prepared in situ from appropriate reactants, although they are preferably made separately and then added to the polymerization reaction mixture.

The macromonomer polymerization process according to the presently claimed invention, in which macromonomers (terminally unsaturated
35 polymers or copolymers) are produced employing the above described oligomeric

chain transfer agents, is suitably carried out at 20 to 200°C, preferably 40-160°C, more preferably 50-145°C.

Any source of radicals or any of the known class of polymerization initiators is suitable, provided the initiator has the requisite solubility in the solvent or monomer mixture chosen and has an appropriate half life at the temperature of polymerization. Polymerization initiators may be redox or thermally or photochemically induced, for example azo, peroxide, peroxyester, or persulfate. Preferably, the initiator has a half life of from about 1 minute to about 1 hour at the temperature of polymerization. Some suitable initiators include ammonium persulfate, azocumene; 2,2'-azobis(2-methyl)butanenitrile; 4,4'-azobis(4-cyanovaleric acid); and 2-(t-butylazo)-2-cyanopropane. Other non-azo initiators having the requisite solubility and appropriate half life may also be used.

The macromonomer polymerization process can be carried out as either a batch, semi-batch, continuous, or feed process. When carried out in the batch mode, the reactor is typically charged with oligomeric chain transfer agent and monomer, or medium and monomer. To the mixture is then added the desired amount of initiator, typically such that the M/I (monomer to initiator) ratio is 10 to 200. In typical examples, the oligomeric chain transfer catalyst is added in the amount such that the catalyst/initiator or C/I ratio is in the range of 0.10 to 20. The mixture is heated for the requisite time, usually one-half hour to ten hours. In a batch process, the reaction may be run under pressure to avoid monomer reflux and the medium can be viewed as absorbing the reaction heat.

If the macromonomer polymerization is to be carried out as a feed system, the reaction may typically be carried out as follows. The reactor is charged with medium, typically an organic solvent. Into a separate vessel are placed the monomer and oligomer. In a separate vessel is added initiator and medium. The medium in the reactor is heated and stirred while the monomer, oligomeric chain transfer agent, and initiator solutions are introduced, for example by a syringe pump or other pumping device. The rate of feed is determined largely by the quantity of solution. When the feed is complete, heating may be continued for an additional half hour or more. Alternatively, all of the oligomeric chain transfer agent may be placed into a reactor with medium initially and monomers and initiator solution added over time.

In either type of process, the macromonomer product may be isolated by stripping off the medium and unreacted monomer or by precipitation

with a non-s lvent. Alternatively, the macromonomer solution may be used as such, if appropriate to its application.

As indicated above, the polymerization can be carried out either in the absence of, or in the presence of, a polymerization medium. Many common
5 organic solvents are suitable as polymerization media. These include aromatic hydrocarbons, such as benzene, toluene and the xylenes; ethers, such as tetrahydrofuran, diethyl ether and the commonly available ethylene glycol and polyethylene glycol monoalkyl and dialkyl ethers, including the Cellosolves and Carbitols; alkyl esters of organic acids and mixed ester-ethers, such as monoalkyl
10 ether-monoalkanoate esters of ethylene glycol. In addition, ketones, such as acetone, butanone, pentanone and hexanone are suitable, as are alcohols such as methanol, ethanol, propanol and butanol. It may be advantageous to use mixtures of two or more solvents. Certain solvents may be preferred for environmental or toxicological reasons.

15 A significant advantage of this method of preparing vinyl terminated macromonomers is that a wide variety of monomers can be polymerized without adversely affecting the molecular weight of the desired macromonomer product. As indicated earlier, typical methods of preparation of vinyl terminated macromonomers are subject to sensitivity to active proton
20 containing monomers. An example would be cobalt porphorine and dioxime catalysts. U.S. Patent 4,680,352 and subsequent patents to Janowicz et al. demonstrate typical examples. Such cobalt catalysts are used extensively to prepare vinyl terminated macromolecules, but have the disadvantage of not working well with hydroxyl and/or carboxyl containing monomer when used at
25 low levels. Also, high level use of these catalysts may produce unacceptable color in the resin. In general, cobalt catalysts are less efficient with acrylate monomers.

After the macromonomer is formed as described above, its solution can be used "as is" or solvent can be optionally stripped off and the backbone
30 monomers are added to the macromonomer along with additional solvent and polymerization catalyst.

According to the present invention, the oligomeric chain transfer agents described above are used to control molecular weight in forming the graft copolymer.

35 Azo type catalysts (0.5-5% by weight on monomer) can be used as can other suitable catalysts such as peroxides and hydroperoxides. Typical of

such catalysts are di-tertiarybutyl peroxide, di-cumylperoxide, tertiaryamyl peroxide, cumenehydroperoxide, di(n-propyl) peroxydicarbonate, peresters such as amyl peroxyacetate and the like. Polymerization is continued usually at the reflux temperature of the reaction mixture until a graft copolymer is formed of the desired molecular weight.

Organic solvents can be used to form the macromonomer or the graft copolymer, for example, aromatics, aliphatics, ketones such as methyl ethyl ketone, isobutyl ketone, ethyl amyl ketone, acetone, alcohols such as methanol, ethanol, n-butanol, isopropanol, esters such as ethyl acetate, glycols such as ethylene glycol, propylene glycol, ethers such as tetrahydrofuran, ethylene glycol mono butyl ether and the like, and as mentioned above, water and mixtures thereof and water miscible solvents.

As indicated above, the graft polymer can be made by copolymerizing the macromonomer in solvent with the rest of the monomer blend, to form a graft copolymer, thereafter neutralizing it and dispersing in water. Solvents can eventually be stripped off after the water dispersion has been formed.

As neutralizing agents for acid groups, suitable inorganic bases include ammonium hydroxide, sodium hydroxide, and potassium hydroxide. Typical amines that can be used as neutralizing agents include amino methyl propanol, amino ethyl propanol, dimethyl ethanol amine, triethylamine, dimethylethanolamine, dimethylaminomethylpropanol and aminomethylpropanol and the like. One preferred amine is amino methyl propanol and the preferred inorganic base is ammonium hydroxide.

Suitable neutralizing agents for amine groups, if used instead of acid groups, include organic or inorganic acids, e.g. acetic acid, formic acid, lactic acid, hydrochloric acid, sulfuric acid, etc.

The conversion of the graft polymer into a water dispersion can be done by admixing the graft polymer solution with an appropriate neutralizing agent and diluting with water, or the polymerized graft copolymer solution can be stirred slowly into a solution of water and the neutralizing agent. The degree of neutralization of the dispersion can be from 10 to 150% of the total amount of reactive groups present, preferably from 80-105%. The final pH of the dispersion can accordingly be about 4-10, preferably 7-10 for an anionic system and 4-7 for a cationic system. Anionic, cationic or non-ionic surfactants can be used, but preferably not, since they might hurt humidity resistance afterwards. As

indicated above, not having to use a surfactant is one of the significant advantages of the present invention.

Preferably, however, the graft copolymer is formed directly into water, wherein the macromonomer is neutralized and dissolved or dispersed into water. The graft copolymer is formed by copolymerizing the rest of the monomer blend (for the backbone) with the macromonomer solution or water dispersion (for the graft or teeth part of the comb or graft copolymer) in the presence of the oligomeric chain transfer agent described above. This procedure has the advantage that less cosolvent should be used in the overall process and solvent stripping can be eliminated. Another advantage is that higher molecular weight graft polymers can be obtained than in solvent polymerization.

Mixtures of suitably compatible macromonomers can be used as long as all are either cationic or anionic in water.

Water-soluble free radical initiators can be used, suitably in the temperature range of 20-98°C, e.g., peroxides, ammonium persulfate, redox initiators such as t-butylhydroperoxide/ascorbic acid. On copolymerizing the monomers with the macromonomer optionally chain transfer agents other than the cobalt chelates can be used as, e.g., mercaptans: mercaptoethanol, t-dodecylmercaptan, N-dodecylmercaptan.

In the synthesis of the graft copolymer, small amounts of difunctional alpha-beta unsaturated compounds can be used as, e.g., ethyleneglycol dimethacrylate or hexanedioldiacrylate. This can result in crosslinked particles.

The overall graft copolymer water borne dispersion should be characterized by an acid or amine value of from 10 to about 150 (mg KOH/g resin solids), more preferably from 15 to about 70, and a hydroxyl number of about 0 to about 250 (mg KOH/g resin solids), more preferably from 40 to 150.

The afore-described binder systems are utilized to produce waterborne coatings by blending with other suitable components in accordance with normal paint formulation techniques.

The graft copolymers of the present invention are useful as film-forming vehicles in the preparation of waterborne coating compositions such as, for example, clearcoat or basecoat compositions useful in automotive applications. The resultant coating compositions have low volatile organic content, preferably to a maximum of 3.50 pounds/gallon.

In preparing coating compositions, according to another aspect of the present invention, the graft copolymer can be combined with a crosslinking agent in the amount of 2 to 50 percent by weight of binder, preferably 10 to 40 percent by weight of binder.

5 Suitable curing agents comprise melamine formaldehyde or alkylated melamine formaldehyde compounds or a blocked or unblocked isocyanate compounds in a one-package system or isocyanate compounds, preferably a water-dispersible polyisocyanate, in a two-package system, or other crosslinking agents such as epoxies, silanes, carbodiimides, etc, able to react with
10 crosslinking functionalities on the graft copolymer.

 If the binder is used in a formulation that is cured with a curing agent containing N-methylol and/or N-methylol ether groups, the curing agent should be dispersed in the water based graft copolymer dispersion to form a stable overall dispersion. Examples of such curing agents are amino resins
15 obtained by reacting an aldehyde, such as formaldehyde, with a compound containing amino group such as melamine, urea and benzoguanamine and total or partial etherification of the N-methylol group with an alcohol such as, e.g., methanol, n-butanol, isobutanol.

 To form a composition which will crosslink under elevated baking
20 temperatures of about 60-180°C for about 5-60 minutes, about 10 to 60%, preferably 10 to 25% by weight, based on the weight of the binder, of a water-soluble water dispersible alkylated melamine formaldehyde crosslinking agent having 1-4 carbon atoms on the alkylated group is preferred.

 These crosslinking agents are generally partially alkylated
25 melamine formaldehyde compounds and may be monomeric or polymeric and if polymeric have a degree of polymerization of about 1-3. Typical alcohols used to alkylate these resins are methanol, ethanol, propanol, butanol, isobutanol, and the like. Preferred alkylated melamine crosslinking agents that are commercially available include Cymel™ 373, 385, 1161, 350, or 1168 (Monsanto) and
30 Resimine™ 714, Resimine™ 730 and 731, Resimine™ 735 and 745 (Cyanamide).

 Coating compositions which contain a melamine crosslinking agent can contain about 0.1 to 1.0%, based on the weight of a binder, of a strong acid catalyst or a salt thereof to lower curing temperatures and time. Paratoluene sulfonic acid is a preferred catalyst or its ammonium salt. Other catalysts that
35 can be used are dodecyl benzene sulfonic acid, phosphoric acid and amine or ammonium salts of these acids.

If the binder is used in a formulation that is cured with a polyisocyanate, a water dispersible polyisocyanate is added to the waterborne graft copolymer dispersion prior to application.

5 The overall dispersion is not stable in this case and should be used within a certain time period. Examples of water dispersable polyisocyanates include biuret and cyclotrimers of hexamethylene diisocyanate, isophorone diisocyanate and tetramethyl xylene diisocyanate. These isocyanates may be modified to such an extent that they contain ionic groups to ease dispersion into water.

10 Typically, a cure promoting catalyst is utilized in conjunction with an isocyanate crosslinking or curing agent. Preferred catalysts are organometallics, suitably dibutyl tin dilaurate, dibutyl tin di-2-ethylhexoate, zinc octoate, zinc naphthenate, vanadium acetyl acetonate, or zirconium acetyl acetonate, in an effective curing amount, typically from about 0.1 to 2% by weight
15 of binder. Such catalysts are optional, for example, elevated temperature and/or time may suffice to cure the composition.

Typical isocyanate crosslinking agents which may be used for curing a coating composition include both compounds and polymers, blocked or unblocked. Examples of suitable polyisocyanates include monomeric
20 polyisocyanates such as toluene diisocyanate and 4,4'-methylene-bis(cyclohexylisocyanate), isophorone diisocyanate and NCO-prepolymers such as the reaction products of monomeric polyisocyanate such as those mentioned above with polyester or polyether polyols. Particularly useful isocyanates are isophorone diisocyanate and the biuret-form
25 1,6-hexamethylene diisocyanate commercially available from Bayer as "Desmodur" N or the like. Other crosslinking agents include 4,4'-biphenylene diisocyanate, tetramethyl diisocyanate, ethylethylene diisocyanate, 1,3-cyclopentylene diisocyanate, 1,3-phenylene diisocyanate, 1,5-naphthalene diisocyanate, bis(4-isocyanatocyclohexyl)methane, and the like.

30 Trifunctional isocyanates may be used, for example, triphenylmethane triisocyanate, 1,3,5-benzene triisocyanate, 2,4,6-toluene triisocyanate, an adduct of trimethylol and tetramethyl xylene diisocyanate sold under the tradename "Cythane 3160," "Desmodur" N 3390 which is the trimer of hexamethylene diisocyanate, and the like. Optionally, one can use a
35 polyisocyanate acrylic copolymer derived from isocyanatoethyl methacrylate

(commercially available as TMI) and the like, as for example disclosed in U.S. Patent 4,965,317 (col. 5) hereby incorporated by reference.

As indicated above, the polyisocyanate may optionally be blocked. Examples of suitable blocking agents are those materials which would unblock at elevated temperatures, for example, lower aliphatic alcohols such as methanol, oximes such as methylethyl ketone oxime, and lactams such as epsiloncaprolactam. Blocked isocyanates can be used to form stable one-package systems. Polyfunctional isocyanates with free isocyanate groups can be used to form two-package room temperature curable systems. In these systems, the product and isocyanate curing agent are mixed just prior to their application.

Other film-forming polymers, preferably 0 to 55 percent by weight (and concomitantly 45 to 100% by weight of the graft copolymer), based on the weight of the binder, may also be used in conjunction with the graft copolymer. Other film forming polymers may be linear or branched and may include acrylics, acrylourethanes, polyesters, polyester urethanes, polyethers, and polyether urethanes that are compatible with the graft polymer.

An organic cosolvent is also typically utilized in the present composition, preferably in minimal amounts, less than 20% by weight of carrier, to facilitate formulation and application of the coating compositions of the present invention. An organic solvent is utilized which is compatible with the components of the composition.

The amounts of graft copolymer, curing agent, and catalyst will, of course, vary widely depending upon many factors, among them the specific components of the composition and the intended use of the composition.

In addition, a composition using the graft copolymers according to the present invention may contain a variety of other optional ingredients, including pigments, pearlescent flakes, fillers, plasticizers, antioxidants, surfactants and flow control agents.

To improve weatherability of a finish produced by the present coating composition, an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers can be added in the amount of about 0.1-5% by weight, based on the weight of the binder. Such stabilizers include ultraviolet light absorbers, screeners, quenchers, and specific hindered amine light stabilizers. Also, an antioxidant can be added, in the about 0.1-5% by weight, based on the weight of the binder.

Typical ultraviolet light stabilizers that are useful include benzophenones, triazoles, triazines, benzoates, hindered amines and mixtures thereof. Specific examples of ultraviolet stabilizers are disclosed in U.S. Patent 4,591,533, the entire disclosure of which is incorporated herein by reference.

5 A coating composition may also include conventional formulation additives such as flow control agents, for example, Resiflow® S (polybutylacrylate), BYK 320 and 325 (high molecular weight polyacrylates); rheology control agents, such as fumed silica, microgels, and non-aqueous dispersion polymers, and the like.

10 When a coating composition is used as a clearcoat (topcoat) over a pigmented colorcoat (basecoat) to provide a colorcoat/clearcoat finish, small amounts of pigment can be added to the clear coat to provide special color or aesthetic effects such as tinting.

Coating compositions can be pigmented and used as the colorcoat, 15 monocoat, primer, or primer surfacer.

The following examples illustrate the invention. All parts and percentages are on a weight basis unless otherwise indicated. All molecular weights disclosed herein are determined by gel permeation chromatography using a polystyrene standard.

20

EXAMPLE 1

This example illustrates the preparation of a methyl methacrylate (MMA) oligomer chain transfer agent synthesis, in which the following components were used.

<u>Ingredients</u>	<u>Parts by Weight</u>
<u>Part 1</u>	
Ethyl Acetate	248.7
Methylmethacrylate (MMA)	499.0
<u>Part 2</u>	
Ethyl Acetate	87.3
Catalyst*	0.87
<u>Part 3</u>	
MMA	1996.0
<u>Part 4</u>	
Vazo™ 52 initiator (DuPont)	19.6
Ethyl Acetate	648.3

*Catalyst = diaquobis(borodifluorodiphenyl-glyoximato) cobaltate (II)

5 A dry reactor equipped with a stirrer, thermocouple, nitrogen positive pressure, and condenser was used. Part 1 was added to the reactor and heated to 80°C. Part 2 was charged to the reactor in a single shot. When the temperature stabilized, Parts 3 and 4 were charged to the reactor over 240 and 300 minutes, respectively. After adding Part 3, the reactor was held at reflux temperature for 30 minutes before cooling.

10

EXAMPLE 2

This example illustrates the preparation of a a macromonomer stabilizer made from methylmethacrylate and methacrylic acid (MMA/MAA) in a 60:40 weight ratio. The following ingredients were used.

15

Ingredients	Parts by Weight
Part 1	
Methyl ethyl ketone (MEK) solvent	1447.40
Methylmethacrylate	577.91
Methacrylic Acid	144.56
Part 2	
MEK solvent	126.32
Vazo™ 67 initiator (DuPont)	3.16
Catalyst*	0.44
Part 3	
Methylmethacrylate	1590.39
Methacrylic Acid	1300.20
Part 4	
MEK solvent	284.22
Vazo™ 67 initiator	18.95
Catalyst*	0.44
Part 5	
MEK solvent	243.25
Vazo™ 52 initiator	9.47
Catalyst*	0.18
Part 6	
MEK solvent	243.25
Vazo™ 52 initiator	9.47
Catalyst*	0.26

*Catalyst = diaquobis(borodifluorodiphenyl-glyoximate) cobaltate (II).

Part 1 was charged to a reactor equipped with stirrer, thermocouple, and nitrogen positive pressure. The reactor was brought to reflux.

5 Parts 2 through 6 were prepared in separate vessels. Part 2 was charged to the reactor in single shot. Parts 3 and 4 were concurrently charged to the reactor at rate of 12.04 and 3.37 g/min, respectively. After adding Part 4, Part 5 was added at a rate of 3.37 g/min. After adding Part 5, the addition of Part 6 was carried out at a rate of 3.37 g/min. (The addition of Part 6 and Part 3 will be complete at

10 the same time.) Following the addition of Parts 3 and 6, the reactor was held at reflux for 30 minutes.

The resulting macromonomer stabilizer (A) was characterized by the following molecular weight data: $M_n = 1405$, $M_w = 2353$, Disp. = 1.68.

EXAMPLE 3

- 5 This example illustrates the preparation of another macromonomer stabilizer, in this case made from MMA/MAA in the ratio of 70:30 by weight. The following ingredients were used.

Ingredients	Parts by Weight
Part 1	
MEK solvent	2233.90
Methylmethacrylate	893.60
Methacrylic Acid	157.80
Part 2	
MEK solvent	183.80
Vazo® 67 initiator (DuPont)	4.61
Catalyst*	0.45
Part 3	
Methylmethacrylate	2886.00
Methacrylic Acid	1462.10
Part 4	
MEK solvent	413.60
Vazo® 67 initiator	27.60
Catalyst*	0.45
Part 5	
MEK solvent	354.20
Vazo™ 52 initiator	13.80
Catalyst*	0.18
Part 6	
MEK solvent	353.98
Vazo® 52 initiator	13.78
Catalyst*	0.27

*Catalyst = diaquobis(borodifluorodiphenyl-glyoximate) cobaltate (II).

Part 1 was charged to a reactor equipped with stirrer, thermocouple, and nitrogen positive pressure. The reactor was brought to reflux. Parts 2 through 6 were prepared in separate vessels. Part 2 was charged to the reactor in a single shot. Parts 3 and 4 were charged concurrently to the reactor at a rate of 18.12 and 4.91 g/min, respectively. At the completion of Part 4 addition, Part 5 was added at a rate of 4.91 g/min. At the completion of Part 5 addition, Part 6 was added at a rate of 4.91 g/min. (The addition of Part 5 and Part 3 will be complete at the same time.) Following the addition of Parts 3 and 5, the reactor was held at reflux for 30 minutes.

This resulted in a macromonomer stabilizer (B) characterized by the following molecular weight data: $M_n = 1206$, $M_w = 2641$, Disp. = 2.19.

EXAMPLES 4-7

These examples illustrate the preparation of self stable graft copolymer emulsions according to the present invention. For forming the backbone, the reactants were 80%, based on the weight of the graft copolymer, of a mixture of styrene (STY), 2-ethylhexylacrylate (2-EHA), methylmethacrylate (MMA) and the MMA oligomeric chain transfer agent in the weight ratio of 23 / 40 / (17-X) / X. For forming the graft or arms of the graft copolymer, the reactants were 20%, based on the weight of the graft copolymer of macromonomers made from MMA and MAA in the weight ration of 12 / 8. The following ingredients were used.

Part	Ingredients	Weight (grams)			
		Ex. 4	Ex. 5	Ex. 6	Ex. 7
1	Demineralized water	789.17	789.17	789.17	789.17
	Macromonomer stabilizer A	55.10	55.10	55.10	55.10
	Triethylamine	25.90	25.90	25.90	25.90
2	Ammonium Persulfate	1.74	1.74	1.74	1.74
	Demineralized water	48.19	48.19	48.19	48.19
3	Demineralized water	880.90	880.90	880.90	880.90
	Macromonomer stabilizer A	220.60	220.60	220.60	220.60
	Triethylamine	108.50	108.50	108.50	108.50
4	Styrene	317.10	317.10	317.10	317.10
	2-Ethylhexylacrylate	551.30	551.30	551.30	551.30
	Methylmethacrylate	234.30	206.70	165.55	131.17
	pMMA Oligomer	0.00	27.50	68.75	103.13
5	Ammonium Persulfate	14.10	14.10	14.10	14.10
	Demineralized water	258.34	258.34	258.34	258.34

- Part 1 was charged into a five liter reactor equipped with stirrer, thermocouple, and nitrogen positive pressure. The mixture was heated to 85°C and purged with nitrogen for 30 minutes. Part 2, 10% of Part 3 and 10% of Part 4 were charged into the reactor in single shot. The reactor temperature was allowed to rise, and once stable the concurrent addition of Parts 3, 4 and 5 to reactor was carried out over 240, 270 and 300 minutes, respectively. After adding Part 5, the temperature in the reactor was held for 60 minutes.

Molecular Weight and Particle Size Data for Examples 4-7			
Example	% pMMA oligomer in Copolymer	Weight Average Molecular Weight	Particle (nm)
4	0 %	77,510	282
5	2 %	48,610	251
6	5 %	25,480	233
7	7.5 %	19,340	336

EXAMPLES 8-9

This example illustrates the preparation of additional graft copolymers according to the present invention, which graft copolymers were the reaction product of 80%, by weight of the graft copolymer components, of STY (23), 2-EHA (40), MMA (17-X), MMA oligomer chain transfer agent (X) and 20%, by weight of the graft copolymer components of MMA (14) and MAA (6) (where the number in parenthesis are the weight ratios in the synthesis. The following ingredients were used.

Part	Ingredients	Weight (grams)	
		Ex. 8	Ex. 9
1	Demineralized water	273.2	181.8
	Macromonomer stabilizer B	19.1	12.7
	triethylamine	6.7	4.5
2	Ammonium Persulfate	0.6	0.4
	Demineralized water	16.7	11.1
3	Demineralized water	505.0	345.0
	Macromonomer stabilizer B	76.4	50.8
	Triethylamine	26.9	17.9
4	Styrene	109.8	73.1
	2-Ethylhexylacrylate	190.9	127.0
	Methylmethacrylate	80.5	29.8
	pMMA Oligomer	0.0	23.8
5	Ammonium Persulfate	4.9	3.3
	Demineralized water	89.5	88.2

10

Part 1 was charged into a two liter reactor equipped with stirrer, thermocouple, and nitrogen positive pressure. The mixture was heated to 85°C and purged with nitrogen for 30 minutes. Part 2, 10% of Part 3 and 10% of Part 4 were charged into the reactor in single shot. The reactor temperature was allowed to increase, and once stable, the concurrent addition of Parts 3, 4 and 5 to the reactor was carried out over 240, 270 and 300 minutes, respectively. After completing the the addition of Part 4, the temperature was held in the reactor for 60 minutes. The results are shown below.

15

Molecular Weight and Particle Size Data for Examples 8-9			
Example	% pMMA oligomer in Copolymer	Weight Average Molecular Weight	Particle (nm)
8	0 %	82,470	233
9	7.5 %	23,340	249

EXAMPLE 10

- 5 This example illustrates a waterborne clearcoat based upon the use of low molecular weight self-stabilized latices utilizing methyl methacrylate oligomer for molecular weight control. The following components were used to prepare the clearcoat:

Component	Amount	Wt. %
Self-stabilized Latex (from Example 7)	12.50	71.43
Triethylamine	0.20	1.14
Butyl Carbitol	0.90	5.14
Butyl Cellosolve	0.90	5.14
Carbodiimide Crosslinker	3.00	17.14
Total	17.50	100.00
Solids (%)	37.0	

- 10 The above components were added in order with mixing. Samples were drawn down over glass to a dry film build of approximately 2.0 mils to produce a clear glossy film. The panels were allowed to cure at 77° F and 50 percent relative humidity. The results were as follows:

	1 Day	2 Day	3 Day	4 Day
Persoz Hardness	36	57	68	82
Swell Ratio	-	3.12	2.5	2.57
Water Spot Resistance*	8	8	10	8

- 15 * Water Spot Ratings were rated on a 1-10 scale with a "10" being perfect. An "8" reflected the fact that the coating swelled but recovered.

EXAMPLE 11

The following formulation for a waterborne clearcoat candidates utilized methylmethacrylate oligomer for molecular weight control:

Component	Amount	Wt. %
Self-stabilized Latex (from Example 4)	25.00	67.20
Triethylamine	0.00	0.00
Water	5.20	13.98
Butyl Cellosolve	2.00	5.38
Carbodiimide Crosslinker	5.00	13.44
Total	37.20	100.00
Solids (%)	37.0	

5

The above components were added in order with mixing. Samples were drawdown over glass to a dry film build of approximately 2.0 mils. The panels were allowed to cure at 77° F and 50 percent relative humidity. The drawdowns with the above solutions produced a clear glossy film with a dust free time of 33 minutes and a tack free time of 4 hr with the following properties:

10

	1 Day	2 Day	3 Day	6 Day	7 Day
Persoz Hardness	20	28	-	40	-
MEK Resistance (double rubs)	-	-	35	-	-

EXAMPLE 12

The following formulation for a waterborne clearcoat was based upon the use of low molecular weight self-stabilized latices utilizing a methylmethacrylate oligomer for molecular weight control:

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Ingredients	Amount	Wt. %
Self-stabilized Latex (from Example 6)	75.00	68.58%
Water	10.00	9.14%
Carbodiimide Crosslinker	24.40	22.30%
Total	109.40	100.00%
Solids (%)	39.0	
Brookfield Viscosity	60	
ICI Viscosity	35	

The sprayout of the above solution resulted in a clear film with very good gloss over a white basecoat.

- 5 of Part 5 hold temperature in reactor for 60 minutes.

Molecular Weight and Particle Size Data for Examples 4-7			
Example	% pMMA oligomer in Copolymer	Weight Average Molecular Weight	Particle (nm)
8	0 %	82470	233
9	7.5 %	23340	249

- 10 Those skilled in the art will no doubt be able to compose numerous variations on the themes disclosed, such as changing the amounts of ingredients insignificantly from those shown, adding innocuous or supplementary substances, or substituting equivalent components for those shown. Such variations are considered to be within the inventive concept, as defined in the following claims.

FA-0643

CLAIMS

What is claimed is:

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1. A composition for a graft copolymer having a molecular weight of 3000 to 500,000 comprising the reaction product of the following:

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- (a) 2 to 98 percent, by weight of the graft polymer, of polymerized ethylenically unsaturated monomers for forming the polymeric backbone of the graft copolymer; (b) 98 to 2%, by weight of the graft polymer, of macromonomers for attachment to said polymeric backbone at a single terminal point of said macromonomer, said macromonomers having an average molecular weight of 500-30,000 and comprising 10 to 100 percent, by weight of the macromonomers, of polymerized alpha-beta ethylenically unsaturated monomers having one of carboxylic-acid functionalities or amine functionalities; and
- (c) 1.0 to 20 percent by weight, based on the weight of the graft copolymer, of one or more terminally unsaturated oligomers having a substantially lower average molecular weight and lower water solubility than the macromonomer of (b) above;

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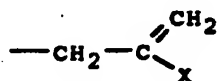
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wherein at least a portion of the carboxylic-acid or amine groups have been neutralized and wherein the macromonomers are soluble or dispersible in an aqueous carrier to stabilize the portion of the graft polymer which forms an insoluble particle and wherein said oligomer has the effect of limiting the molecular weight of the graft copolymer.

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2. The composition of claim 1 wherein the oligomer, or a molecular weight distribution of oligomers, has the following end group:

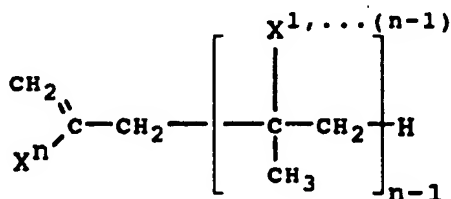


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where X is -CONR₂, -COOR, OR¹, -OCOR, -OCOOR¹, -NRCOOR¹, halo, cyano, or a substituted or unsubstituted phenyl or aryl, wherein each R is independently selected from the group consisting of hydrogen, silyl, or a substituted or unsubstituted alkyl, alkyl ether, phenyl, benzyl, and aryl, wherein

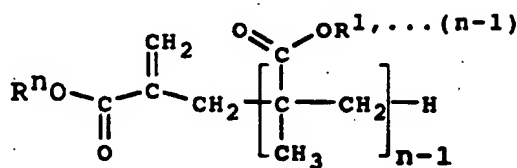
substituted means with a substituent selected from the group consisting of epoxy, hydroxy, isocyanato, cyano, amino, silyl, acid, halo, or acyl; and wherein R^1 is the same as R except not H; and wherein each alkyl is independently selected from the group consisting of branched or unbranched hydrocarbons having 1 to 12 carbon atoms or cyclical hydrocarbons having 4 to 12, preferably 5 to 6 carbon atoms; and halo or halogen is bromo, iodo, chloro or fluoro; except excluding the use of a pure dimer when X is substituted or unsubstituted phenyl or aryl.

3. The composition of claim 2, wherein said oligomer, or molecular weight distribution of oligomers, has the following formula:



wherein n is on average 2 to 100 and X^1 to X^n are independently X as defined above.

4. The composition of claim 1, wherein said oligomer, or molecular weight distribution of oligomers, has the following formula:



wherein n is, on average, 2 to 20 and R^1 to R^n are each independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, alkyl ether, phenyl, benzyl, or aryl, which substituent is selected from the group consisting of epoxy, hydroxy, isocyanato, cyano, amino, silyl, acid, anhydride, halo, or acyl; and each alkyl is independently selected from the group consisting of branched, unbranched, or cyclical hydrocarbons having 1 to 12 carbons, halo is selected from the group consisting of bromo, iodo, chloro and fluoro, and silyl is

-SiR²(R³)(R⁴), wherein R², R³, and R⁴ are independently alkyl, phenyl, alkyl ether, or phenyl ether, wherein alkyl is as defined above.

5 5. The composition of claim 1, wherein the oligomer is comprised of alkyl methacrylate wherein the alkyl has 1 to 10 carbon atoms.

10 6. The composition of claim 1, wherein said macromonomers comprise between 10 and 40% by weight, based on the weight of said macromonomer, of polymerized ethylenically unsaturated monomers containing carboxylic-acid functionality.

15 7. The composition of claim 1, wherein said macromonomers further comprise between 5 and 30% by weight, based on the weight of said macromonomer, of polymerized ethylenically unsaturated monomers containing hydroxyl functionality.

20 8. The composition of claim 1, wherein said backbone further comprises polymerized ethylenically unsaturated monomers which are predominantly acrylate and/or styrene selected from the group consisting of alkyl acrylates, cycloaliphatic acrylates, aryl acrylates, styrene, alkyl styrene, and mixtures thereof; and wherein the ethylenically unsaturated monomers containing carboxylic-acid functionality comprise monomers selected from the group consisting of carboxylic alkyl acrylates, wherein the above-mentioned alkyl, cycloaliphatic, and aryl groups have 1 to 12 carbon atoms, and wherein the
25 macromonomers are predominantly methacrylates analogous to the above.

9. A coating composition comprising the graft copolymer of claim 1.

30 10. A method of preparing a graft copolymer having a molecular weight of 3000 to 500,000, comprising reacting simultaneously, in an aqueous solvent, the following components:

35 (a) 2 to 98 percent, by weight of the graft polymer, of polymerized ethylenically unsaturated monomers for forming the polymeric backbone of the graft copolymer;

- 5 (b) 98 to 2%, by weight of the graft polymer, of macromonomers for attachment to said polymeric backbone at a single terminal point of said macromonomer, said macromonomers having an average molecular weight of 500-30,000 and comprising 10 to 100 percent, by weight of the macromonomers, of polymerized alpha-beta ethylenically unsaturated monomers having one of carboxylic-acid functionalities or amine functionalities; and
- 10 (c) 1.0 to 20 percent by weight, based on the weight of the graft copolymer, of one or more terminally unsaturated oligomers having a substantially lower average molecular weight and lower water solubility than the macromonomer of (b) above;
- 15 wherein at least a portion of the carboxylic-acid or amine groups have been neutralized and wherein the macromonomers are soluble or dispersed in an aqueous carrier to stabilize the portion of the graft polymer which forms an insoluble particle and wherein said oligomer has the effect of substantially reducing the molecular weight of the graft copolymer.